

# Effects of In Situ Conditions on Aquifer Capacity for CO<sub>2</sub> Sequestration in Solution

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## INTRODUCTION

Geological sequestration of CO<sub>2</sub> is an option for reducing CO<sub>2</sub> emissions into the atmosphere that is technologically feasible as a result of the experience gained in the energy and chemical industries with deep injection of waste and hazardous fluids. Carbon dioxide can be geologically sequestered in sedimentary basins by: stratigraphic and structural trapping in depleted oil and gas reservoirs; solubility trapping in reservoir oil and formation water; adsorption trapping in uneconomic coal beds; cavern trapping in salt structures; and mineral immobilization (Bachu, 2001, and references therein). All these trapping mechanisms lead to carbon sequestration because the CO<sub>2</sub> is not released back into the atmosphere unless it is produced. Use of CO<sub>2</sub> in enhanced oil and gas recovery (EOR and EGR), and in enhanced coalbed methane recovery (ECBMR) represents forms of both geological sequestration and storage, because a significant proportion of the injected CO<sub>2</sub> is produced back at the pump and has to be captured, separated and re-circulated back into the system (e.g., Holtz et al., 2001; Koide & Yamazaki, 2001). Hydrodynamic trapping in deep aquifers (Bachu et al., 1994) is similar to EOR and ECBMR because ultimately carbon will be released back into the atmosphere at aquifer discharge unless it has dissolved in formation water. The retention time of these forms of CO<sub>2</sub> sequestration and storage varies between a few months to potentially millions of years, depending on flow paths and processes.

Use of CO<sub>2</sub> in EOR, EGR and ECBMR, although the most economic, will not reduce significantly CO<sub>2</sub> emissions into the atmosphere. Although the cheapest, CO<sub>2</sub> sequestration in depleted reservoirs will likely extend over a long period of time and will not provide sufficient capacity in the short-to-medium term, because many oil and gas reservoirs are still producing and are not immediately available. Sequestration in salt caverns is not likely to be implemented, except maybe for some very specific cases, because of its high cost. Compared with the previous options, sequestration of CO<sub>2</sub> in deep saline aquifers is considered as having by far the largest potential capacity, on the order of 1000 Gt (Gunter et al. 1998), because of the extremely large volume of pore space in sedimentary basins. Although it does not bring an economic benefit, it is likely to be implemented early on because it provides the necessary capacity and, in some instances, because of need, availability and accessibility (Gale et al., 2001). Carbon dioxide injected into deep saline aquifers will exist initially as a CO<sub>2</sub> plume, but will dissolve into the formation water over a long period of time (McPherson & Cole, 2000), until the water reaches saturation. The amount of CO<sub>2</sub> that will ultimately dissolve in formation water depends on aquifer characteristics such as pressure, temperature and salinity.

## ULTIMATE CO<sub>2</sub>-SEQUESTRATION CAPACITY IN SOLUTION

Two approaches have been used previously to estimate the CO<sub>2</sub>-sequestration capacity in an aquifer. The “reservoir-engineering” approach assumes that the injected CO<sub>2</sub> as a separate phase simply displaces the formation water in the pore space, similar to the oil displacement by CO<sub>2</sub>-flooding in an enhanced oil recovery operation. Capacity estimates are based on reservoir-scale numerical simulations, which show that, depending on simulation time scale and flow distance, a significant amount of the injected CO<sub>2</sub> will dissolve in the formation water at the edge of the CO<sub>2</sub> plume. This amount can vary between 30% for flow at the reservoir scale (Law & Bachu, 1996) and 100% for flow at the basin scale (McPherson & Cole, 2000). The other approach considers that dissolution is the primary method of CO<sub>2</sub> sequestration, and capacity estimates are based on simple volumetric calculations. Assuming that between 1% and 6% of aquifer area can be used for CO<sub>2</sub> sequestration, capacity calculations then consider a CO<sub>2</sub> concentration of 40-60 kg CO<sub>2</sub>/m<sup>3</sup> solution to estimate aquifer CO<sub>2</sub>-sequestration capacity (Bergman & Winter, 1995; Bradshaw & Rigg, 2001; Holt et al., 1995; Koide et al., 1992; 1995). To date, both displacement and

dissolution approaches have considered only non-reactive conditions (i.e., no geochemical reactions take place concurrent with CO<sub>2</sub> injection, flow and dissolution).

A more realistic and rigorous approach is to consider that the injected CO<sub>2</sub> will dissolve in formation waters up to saturation, and that mineral precipitation will take place concurrently or after saturation, depending on local conditions and kinetics of the processes involved. Assuming that CO<sub>2</sub> dissolution is relatively much faster than carbonate precipitation (Gunter et al., 1993), it is possible to decouple the two processes, and consider only solubility trapping as the main mechanism for CO<sub>2</sub> sequestration in aquifers in the short-to-medium term (i.e., non-reactive physical processes control CO<sub>2</sub> sequestration capacity). The injected CO<sub>2</sub> in excess of saturation and/or precipitation will continue to flow as a separate phase in a plume driven by buoyancy and aquifer hydrodynamics, until it will eventually either exhaust itself, will be trapped into geological traps, or will leak back into the atmosphere.

In a deep saline aquifer, an aqueous inorganic carbon system is primarily controlled by dissolved CO<sub>2</sub> in the water and interaction with carbonate and siliciclastic minerals. Ideally, the total inorganic carbon (TIC) content of formation water should be measured for in situ conditions, but no direct in situ measurements of TIC or pH have been documented and complete water and mineralogical analyses are usually done only for small study areas within a sedimentary basin. Formation water samples routinely taken by the petroleum industry are analyzed for major ions at laboratory conditions and can be used to estimate total inorganic carbon content in an aquifer. The lack of complete chemical analyses that quantify the minor species, which act as buffers, in the water requires that two assumptions be made to practically calculate TIC: *no non-carbonate buffers exist in the system* and *the aquifer is non-reactive*. These two assumptions mean that the alkalinity or acid buffering capacity is controlled only by carbonate species and that addition of CO<sub>2</sub> to a system will cause the amount of carbon to increase, but no dissolution or precipitation of carbonate minerals will occur. These assumptions will generate a conservative estimate of capacity if non-carbonate buffers truly exist in the water; however, if only carbonate species control the pH, then the opposite is true, the capacity will be overestimated, because the addition of CO<sub>2</sub> to an aquifer will result in dissolution of carbonate minerals, thereby reducing the available capacity for further dissolved CO<sub>2</sub> in water. The benefit of these assumptions is that the capacity calculation is simplified to the difference between the maximum solubility of CO<sub>2</sub> and the existing total inorganic carbon in the formation water. Thus, the *Ultimate CO<sub>2</sub>-Sequestration Capacity in Solution (UCSCS)* of an aquifer is the difference between the maximum capacity and the current carbon content in solution in that aquifer and is expressed mathematically by (Bachu & Adams, 2003):

$$UCSCS = \iiint \varphi(\rho_S X_S^{CO_2} - \rho_0 X_0^{CO_2}) dx dy dz \quad (1)$$

where  $\varphi$  is porosity,  $\rho$  is the density of formation water,  $X^{CO_2}$  is carbon content (mass fraction), and the subscripts 0 and S stand for current and at saturation, respectively. The mass fraction of CO<sub>2</sub> at saturation,  $X_S^{CO_2}$ , is a function of formation water salinity, temperature and pressure. In this formulation it is assumed that the pore space is water saturated ( $S_w=1$ ).

The CO<sub>2</sub> solubility at saturation in formation water,  $X_S^{CO_2}$ , depends on pressure, temperature and salinity. The mole fraction of CO<sub>2</sub> at saturation in freshwater can be calculated according to the Krichevsky-Kasarnovsky equation, on the basis of aquifer temperature and pressure, fugacity of pure-phase CO<sub>2</sub>, molar volume of CO<sub>2</sub> at infinite dilution, and Henry's constant (Enick & Klara, 1990). The last two parameters can be evaluated on the basis of relationships developed by Enick and Klara (1990) for the temperature range 298 K to 523 K (25°C to 250°C) and pressures from 3.4 MPa to 72.4 MPa. The fugacity of the pure-phase CO<sub>2</sub> is calculated from equations of state (Span & Wagner, 1996). The reduction in CO<sub>2</sub> solubility as a result of the presence of dissolved solids in formation water (salting out effect) is estimated according to a correlation developed by Enick and Klara (1990), which is valid for a wide range of temperatures and pressures.

The current carbon content in formation water,  $X_0^{CO_2}$ , is more difficult to estimate. Carbon dioxide dissolves in water and generates a weak carbonic acid, which subsequently dissociates into  $HCO_3^-$  and  $CO_3^{2-}$ . Thus, for non-reactive conditions, the total carbon content,  $C_T$ , which is the sum of these species, can be calculated according to:

$$C_T = (H_2CO_3^*) + (HCO_3^-) + (CO_3^{2-}) \quad (2)$$

where (...) denotes concentration, and, by convention, the dissolved  $CO_2$  and the carbonic acid are lumped together and denoted by  $H_2CO_3^*$ . The concentration of bicarbonate and carbonate ions ( $HCO_3^-$  and  $CO_3^{2-}$ ) in formation water is usually measured, and the concentration of  $H_2CO_3^*$  can be estimated on the basis of the relations between the activity, denoted by [...], of these species at equilibrium:

$$K_1 = [HCO_3^-] \cdot [H^+] / [H_2CO_3^*]$$

$$K_2 = [CO_3^{2-}] \cdot [H^+] / [HCO_3^-] \quad (3)$$

and the relations between concentration and activity for each species:

$$[X] = \gamma_X \cdot (X) \quad (4)$$

In the above relations,  $K_i$  are equilibrium constants for each reaction that vary with temperature and pressure,  $X$  is any chemical species and  $\gamma_X$  is its corresponding activity coefficient. The latter can be estimated using the extended Debye-Hückel equation for low ionic strength solutions, usually less than 1.0, which is the practical limit of the extended Debye-Hückel equation (Kharaka et al., 1989). This limit corresponds to a salinity of ~58,000 mg/l  $NaCl_{(aq)}$ . For saline waters that have ionic strengths greater than 1, the Pitzer equations may be required for calculating the effective concentration of dissolved salts. However, lack of virial coefficient data limits the use of the Pitzer equations to temperatures up to 74.5°C.

The water composition, pH,  $CO_3$ ,  $HCO_3$  and alkalinity reported in formation water analyses are not representative for in situ conditions, because water samples are analyzed at surface conditions, most often long after sampling, by which time a large proportion of dissolved gases have been lost. To evaluate these, a realistic assumption is to consider that the formation water sample was originally in geochemical equilibrium with the formation rocks, particularly with carbonate minerals such as calcite or dolomite (most likely calcite), owing to the very rapid equilibration of water with these minerals. Thus, if the rock mineralogy is known, geochemical speciation models, such as Solmineq (Kharaka et al., 1989), can be used to calculate the composition of the sampled formation waters at in situ conditions, resulting in more accurate values for pH,  $CO_3^{2-}$  and  $HCO_3^-$  and for the current carbon content  $X_0^{CO_2}$ .

The density of formation water saturated with  $CO_2$ ,  $\rho_s$ , needs also to be estimated for the determination of the ultimate  $CO_2$ -sequestration capacity in solution in an aquifer. The density of freshwater density increases only slightly (<3%) when  $CO_2$  is dissolved, and the solubility of  $CO_2$  decreases significantly when other ions are present in solution (Enick & Klara, 1990); hence the increase in formation water density is expected to be relatively small. Because the contribution of dissolved gases, including  $CO_2$ , is very small and usually is negligible by comparison with the increase in density of formation water when salinity increases, there are no data and relations in the literature for calculating the density of formation water containing  $CO_2$ . Bachu & Adams (2003) arrived at the following expression for the density of  $CO_2$ -saturated formation water,  $\rho_b^{CO_2}$ :

$$\rho_b^{CO_2} = \frac{\rho_b}{1 - X^{CO_2} \left(1 - \frac{V_\phi}{M_2} \rho_w\right)} \quad (5)$$

where  $\rho_w$  and  $\rho_b$  are the densities of pure water and brine, respectively,  $M_2$  is the molecular weight of the solute ( $M_2=44.01$  g/mol for  $\text{CO}_2$ ),  $X^{\text{CO}_2}$  is the  $\text{CO}_2$  mass fraction, and  $V_\phi$  is the apparent molar volume of  $\text{CO}_2$  in pure water, given by Garcia (2001):

$$V_\phi = 37.51 - 9.585 \cdot 10^{-2} T + 8.740 \cdot 10^{-4} T^2 - 5.044 \cdot 10^{-7} T^3 \quad (6)$$

After analyzing several published algorithms for calculating water density, Adams and Bachu (2002) recommend using the expressions presented by Batzle and Wang (1992) to calculate the density of fresh and saline water,  $\rho_w$  and  $\rho_b$ , for the range of temperature 20-350°C, pressure 5-100 MPa and salinities of up to 320,000 mg/l.

Aquifer geometry (depth and thickness) and porosity, and formation water pressure, temperature, salinity and density in the aquifer can be determined using data collected by the energy industry in the process of hydrocarbon exploration (Bachu, 2002). In addition, using relations (2)-(4) for the current total inorganic carbon content in formation water, the relations presented by Enick & Klara (1990) for  $\text{CO}_2$  content at saturation, and relations (5)-(6) for estimating the density of formation water containing  $\text{CO}_2$ , it is possible to calculate the ultimate capacity for  $\text{CO}_2$  sequestration in solution, UCSCS, in an aquifer or any region thereof using relation (2) and standard mapping procedures.

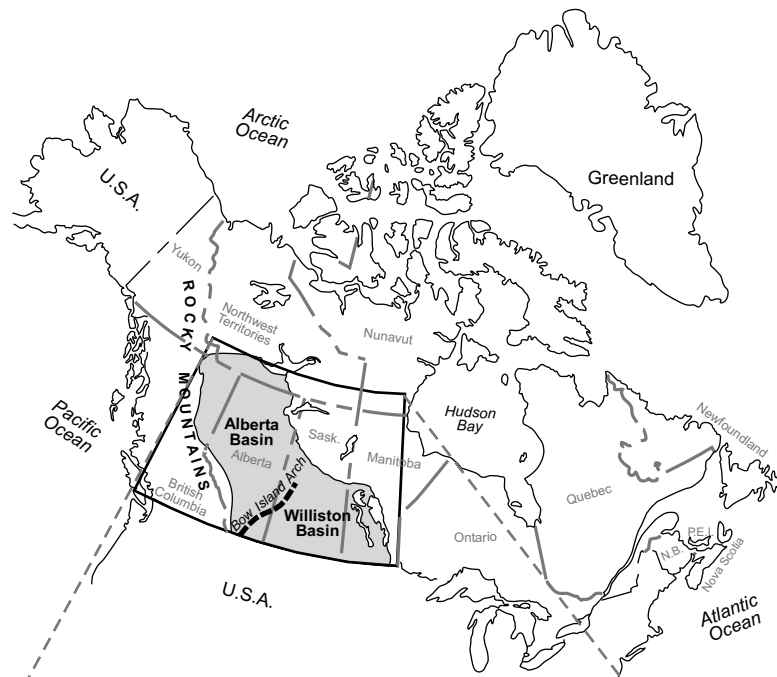
## **$\text{CO}_2$ -SEQUESTRATION CAPACITY IN SOLUTION IN THE WINNIPEGOSIS AQUIFER**

The Western Canada Sedimentary Basin, comprising the Alberta basin and the Canadian part of the Williston basin (Figure 1a), is a large energy producer. Approximately 60% of  $\text{CO}_2$  emissions (~150 Mt/yr) are produced at large, stationary point sources such as thermal power plants, refineries, oil sands, petrochemical and cement plants, and pulp mills. The basin is generally well suited for geological sequestration of  $\text{CO}_2$  because  $\text{CO}_2$  can be sequestered or stored by all means and it meets all the basin-scale criteria, such as tectonic stability, favorable geology and hydrogeology, abundance of oil and gas reservoirs, presence of extensive coal and salt beds, maturity and well-developed infrastructure (Bachu & Stewart, 2002). The estimated sequestration capacity of depleted oil and gas pools, currently on the order of 300 Mt  $\text{CO}_2$ , is insufficient to cover immediate  $\text{CO}_2$  sequestration needs, even if additional oil and gas pools will reach depletion in the next few years. Enhanced oil and coalbed methane recovery are still in the stage of implementation and technological development, respectively. Thus,  $\text{CO}_2$  sequestration in deep saline aquifers is likely to be implemented concurrently with other sequestration means.

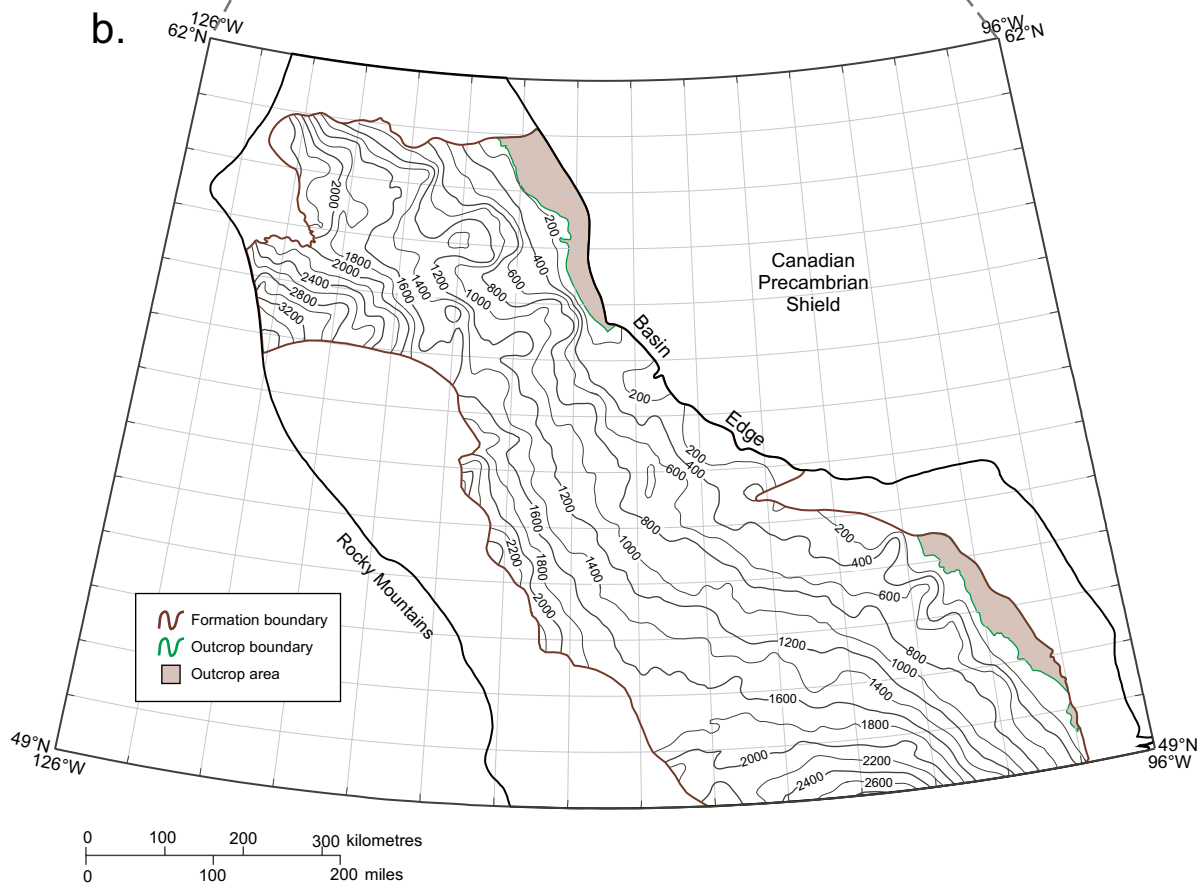
The Middle Devonian Winnipegosis Formation, covering an area of approximately 1,000,000 km<sup>2</sup> (Figure 1b), was deposited during the platform-margin stage of basin evolution and consists mainly of dolostones, with minor limestones present. The Winnipegosis Formation forms an aquifer confined by shaly aquitards and evaporitic aquicludes. The formation dips from zero depth at outcrop near and at the basin's shallow edge in the east, to more than 3400 m depth in the northwest, 2200 m in the southwest, and 2800 m in the south (Figure 1b). The aquifer has an average thickness of 45 m (Figure 2a). Well-scale porosity varies from less than 5% in the carbonate platform to more than 20% in carbonate reefs (Figure 2b).

Relevant properties of the formation water and injected  $\text{CO}_2$  at in situ conditions were calculated according to the procedure described by Bachu (2002) on the basis of 1382 good quality drillstem tests and 842 water analyses. Pressure in the aquifer is controlled mainly by depth, the aquifer being generally at sub-hydrostatic to hydrostatic conditions, and reaches up to 30 MPa. Temperature at the top of the aquifer varies from 5°C at outcrop to 130°C at its deepest in the west (Figure 3a). Water salinity in the Winnipegosis aquifer is high, reaching close to 280 g/l in central Alberta (Figure 3b) as a result of original seawater salinity altered by diagenesis and salt dissolution from the overlying halite Prairie Formation. The aquifer has not been flushed with meteoric water, except for shallow regions, where meteoric water reaches the aquifer and salinity is as low as 5 g/l. Water density, calculated using a direct regression-line relationship and adjusted for in situ conditions (Adams & Bachu, 2002), varies between

a.



b.



**Figure 1. Location and depth (m) of the carbonate Winnipegosis Formation in the Western Canada Sedimentary Basin.**

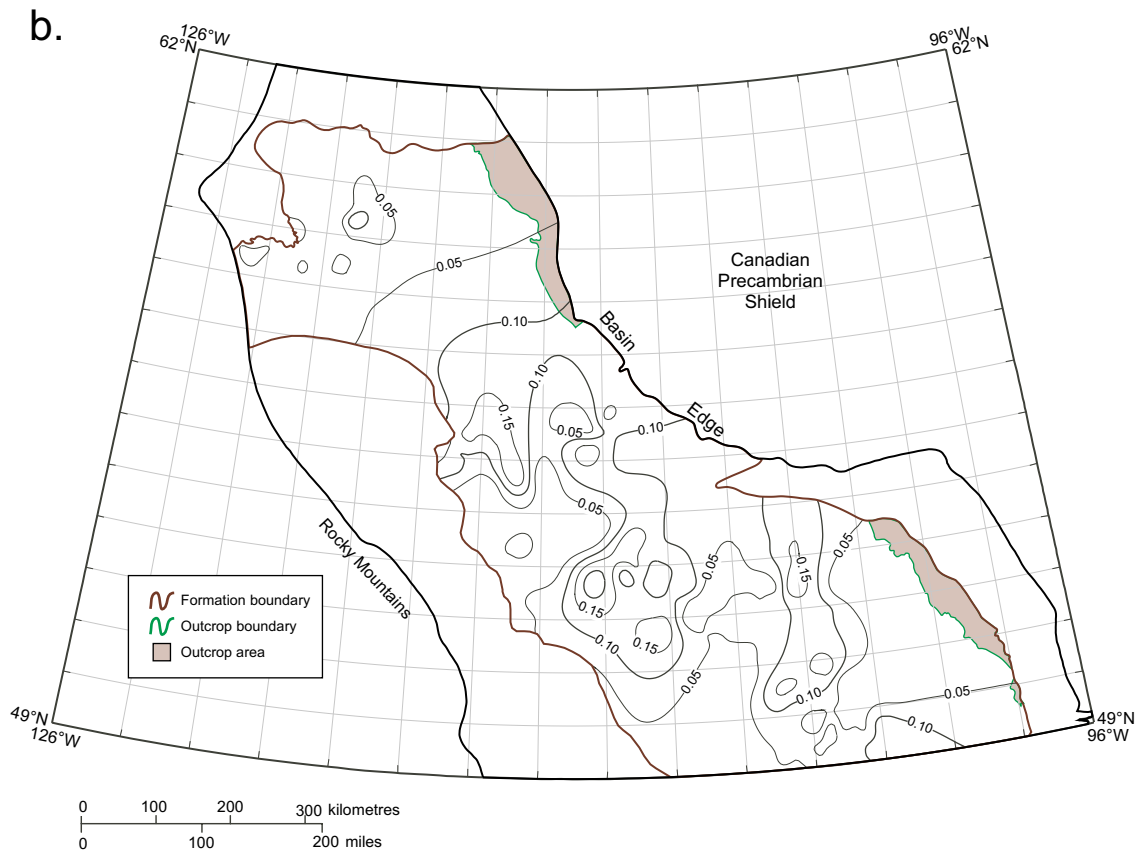
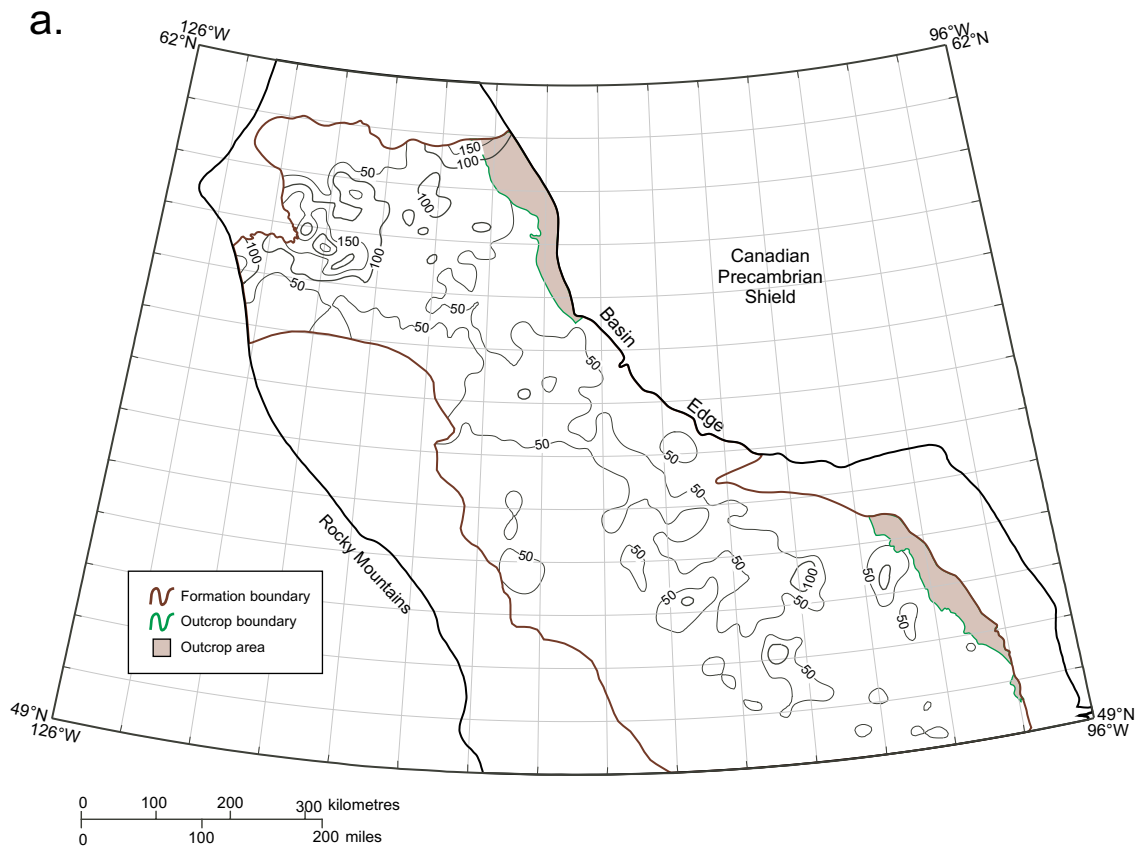
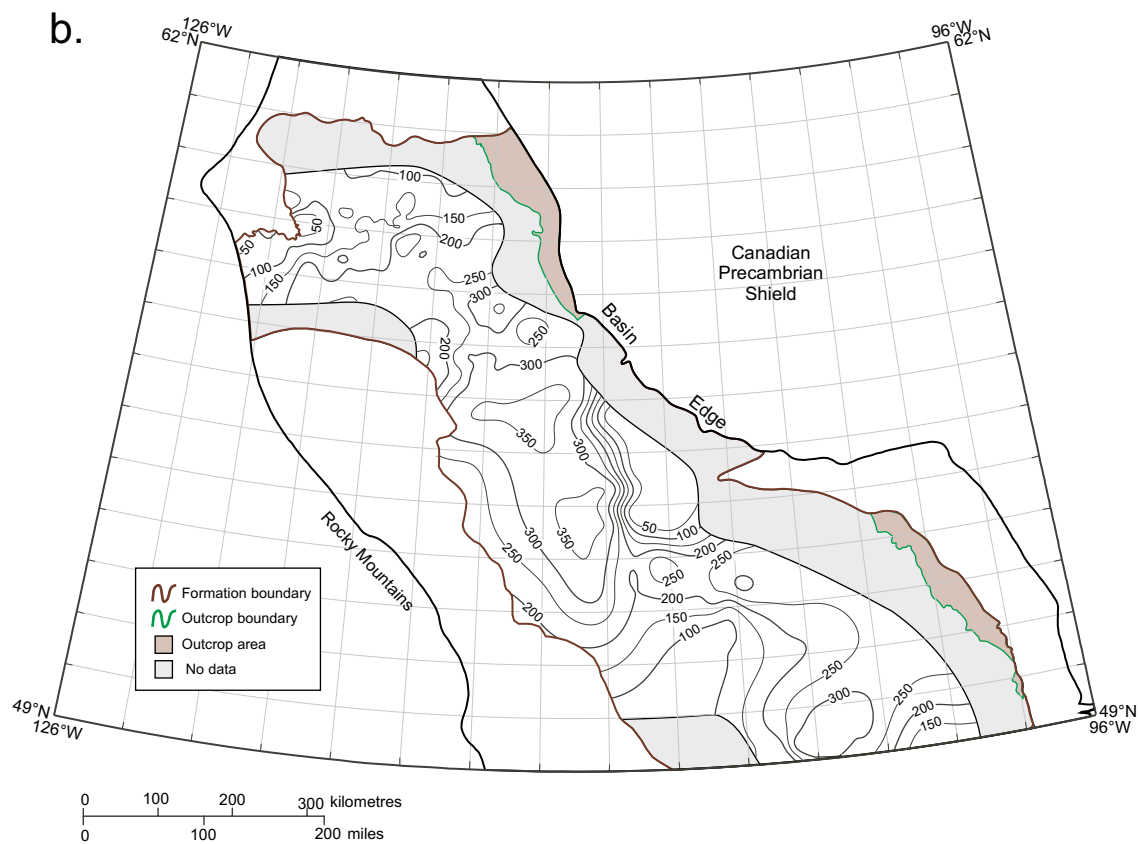
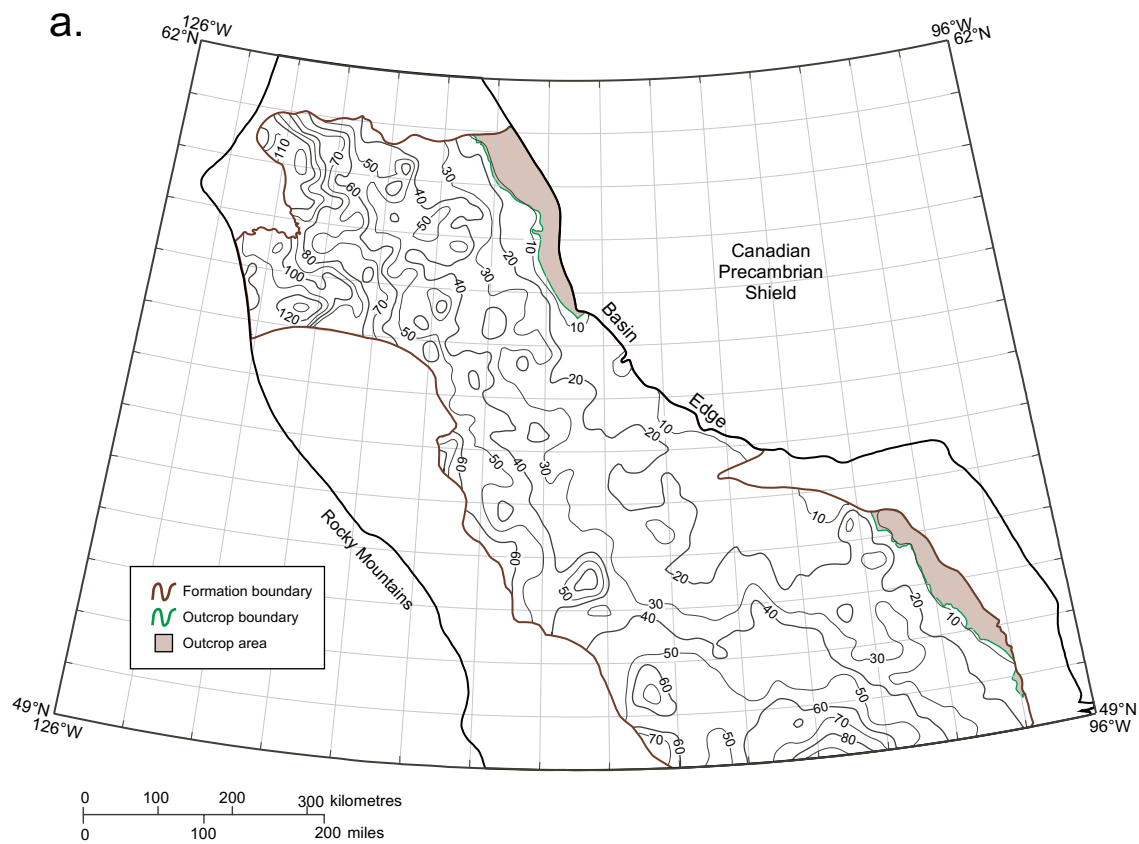


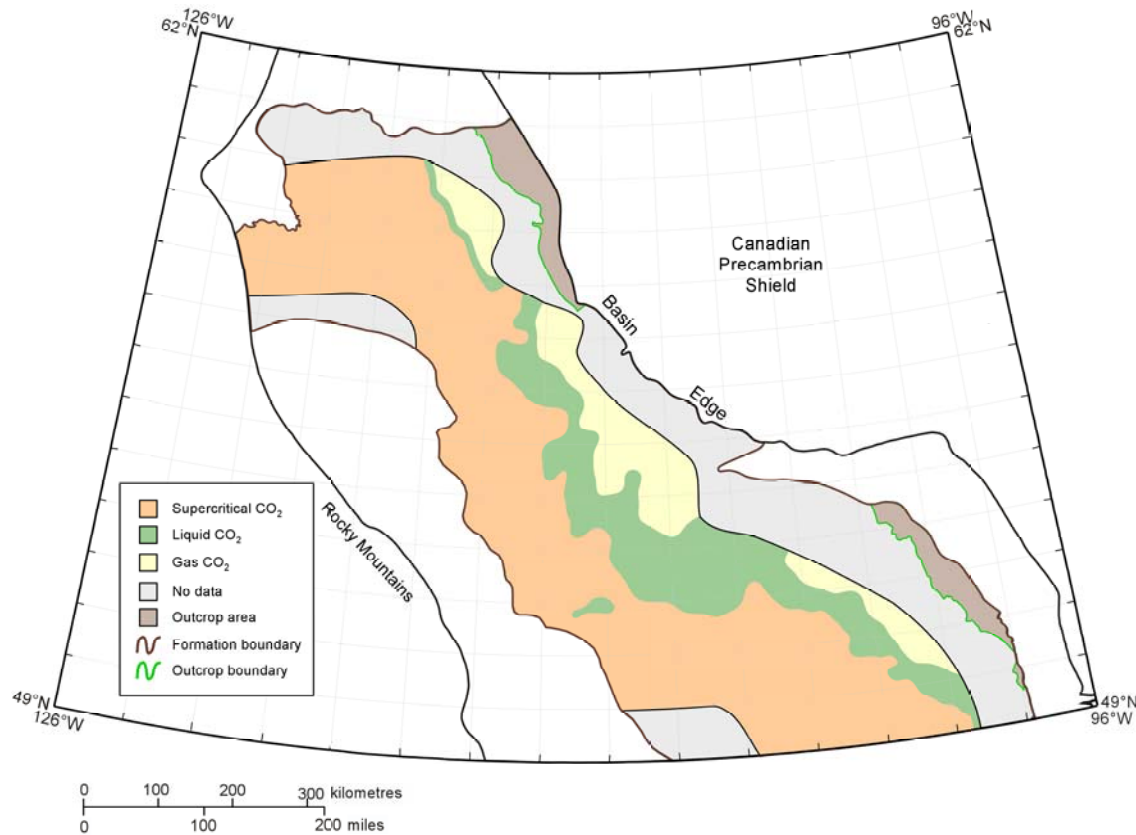
Figure 2. Characteristics of the Winnipegosis aquifer: a) isopach (m), and b) porosity.



**Figure 3. Characteristics of formation water in the Winnipegosis aquifer: a) temperature (°C), and b) salinity (g/l).**

less than  $990 \text{ kg/m}^3$  in shallow, low-salinity areas, to more than  $1260 \text{ kg/m}^3$  at the center of the high-salinity plume.

If  $\text{CO}_2$  is injected into the Winnipegosis aquifer, it will be a dense fluid (liquid or supercritical, Figure 4), in most of the aquifer, except along the eastern shallow edge of the basin. The region that meets the criteria for  $\text{CO}_2$  injection (Bachu, 2000; 2003) covers an area of  $615,500 \text{ km}^2$ . In this area,  $\text{CO}_2$  density at in situ conditions varies between  $170 \text{ kg/m}^3$  and more than  $850 \text{ kg/m}^3$ . Because the density of the dense-fluid  $\text{CO}_2$  decreases, rather than increases, with depth in a cold basin (Bachu, 2002; 2003), the highest density of free-phase  $\text{CO}_2$  ( $>750 \text{ kg/m}^3$ ) is attained in the central and southern parts of the aquifer, rather than in the southwest, where temperature effects lead to a decrease in  $\text{CO}_2$  density as aquifer depth increases.

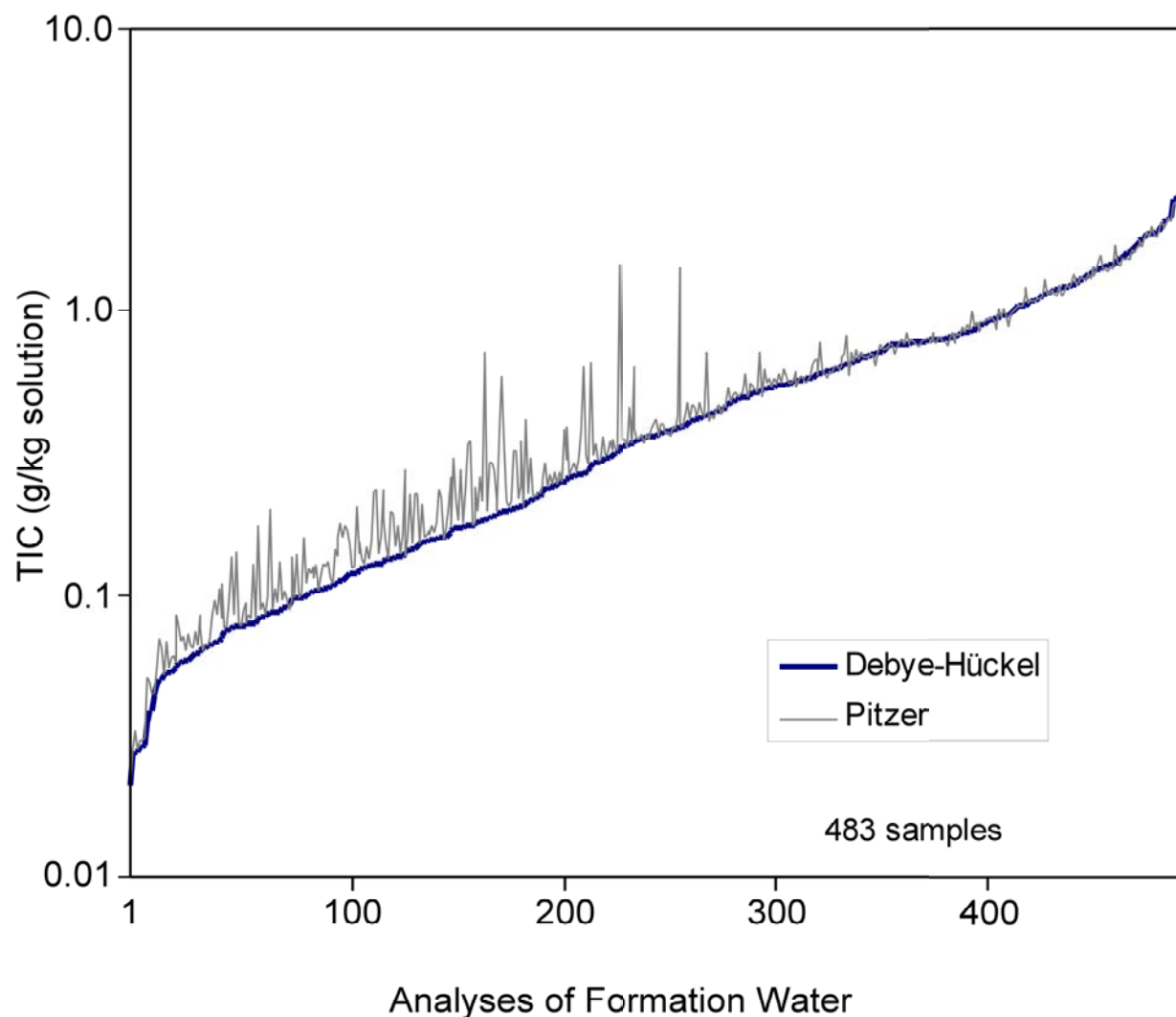


**Figure 4. Estimated  $\text{CO}_2$  phase at the top of the Winnipegosis aquifer.**

For TIC calculations, the aquifer was assumed to contain no non-carbonate buffers and to be non-reactive, because water analyses document only major ion concentrations, TDS values and pH at laboratory conditions. The current TIC was calculated for in situ conditions assuming equilibrium with calcite and using both Pitzer and the extended Debye-Hückel equations. Of the 842 water analyses, 164 did not equilibrate at in situ conditions using the Debye-Hückel equations, indicating an error in the respective water analyses. In situ equilibrium conditions could not be calculated for 327 analyses using the Pitzer equations because either they did not equilibrate or the temperature was beyond the validity range of the Pitzer equations. The in situ equilibrium conditions could be calculated using both Pitzer and Debye-Hückel equations for 483 water analyses.

The TIC at in situ conditions calculated using the Debye-Hückel equations varies between 0.02 and 9.34 g/kg solution, with an average of 0.71 g/kg solution, which correspond, respectively, to 0.025, 10.24 and  $0.79 \text{ kg/m}^3$  solution. The Pitzer equations generally predict higher TIC than the Debye-Hückel

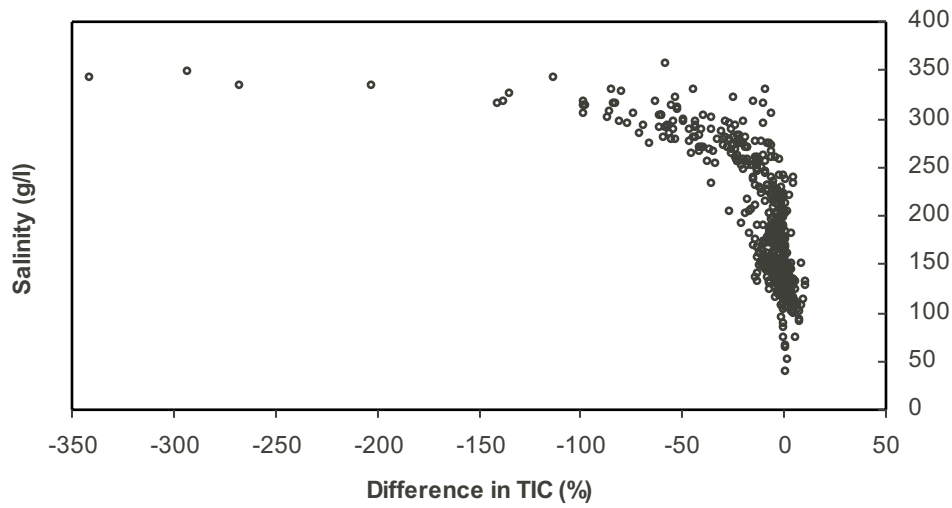
equations, because, for saline waters, Pitzer equations more accurately determine activity coefficients and are limited only by the availability and range of laboratory data for individual species. For comparison, Figure 5 shows histograms of the TIC in Winnipegosis formation water calculated using both Debye-Hückel and Pitzer equations. The differences are significant for low-TIC water (generally <0.8 g/kg solution), and become insignificant for high TIC water. The relative difference,  $(TIC_{DH} - TIC_P)/TIC_{DH}$ , in percent, between in situ TIC calculated with the Debye-Hückel and Pitzer equations ( $TIC_{DH}$  and  $T_P$ , respectively) is shown in Figure 6 as a function of aquifer-water salinity, temperature and pressure. It is evident that temperature and pressure are not critical in estimating TIC using one or the other of the two geochemical speciation models, but salinity is. Both Debye-Hückel and Pitzer equations predict equilibrium conditions that lead to close TIC values for relatively low salinity water (TDS < 100 g/l), and diverge significantly (differences > 20%) as salinity increases over ~250 g/l. This is because high-salinity waters have ionic strength greater than the theoretical limit of validity for the Debye-Hückel equation. As ionic strength increases past its theoretical limit, Debye-Hückel activity coefficients continue to decrease, whereas Pitzer values begin to increase according to experimental observations.



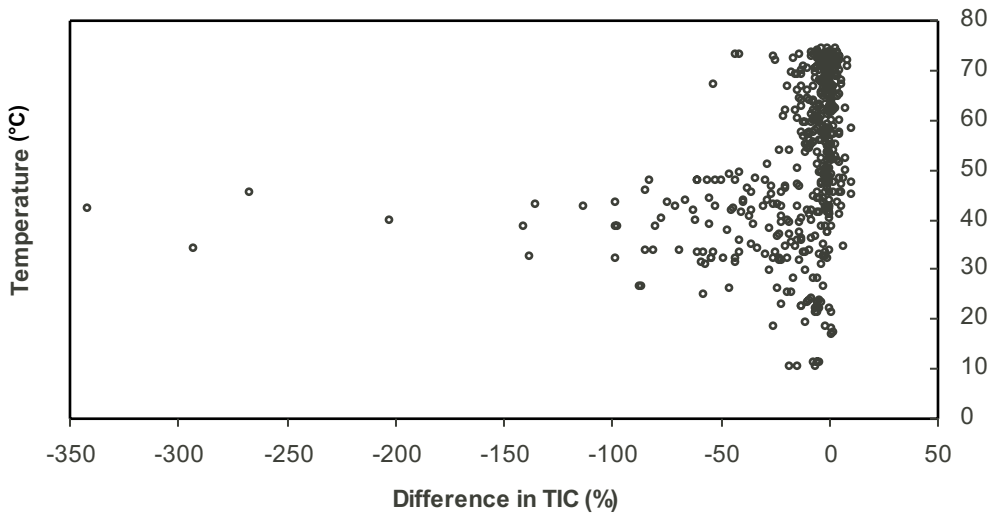
**Figure 5. Current total inorganic carbon (TIC) in formation water in the Winnipegosis aquifer, estimated at in situ conditions using Debye-Hückel and Pitzer geochemical speciation models.**

Bringing the water analyses from surface to in situ conditions leads to a slight increase in salinity (<1%), almost negligible, particularly for high-salinity water. The CO<sub>2</sub> solubility at saturation is 1 to 3 orders of magnitude greater than the current TIC, varying between 14.6 and 71 g/kg solution, with an average of 24.7 g/kg solution. The UCSCS in formation water for the Winnipegosis aquifer was calculated using the

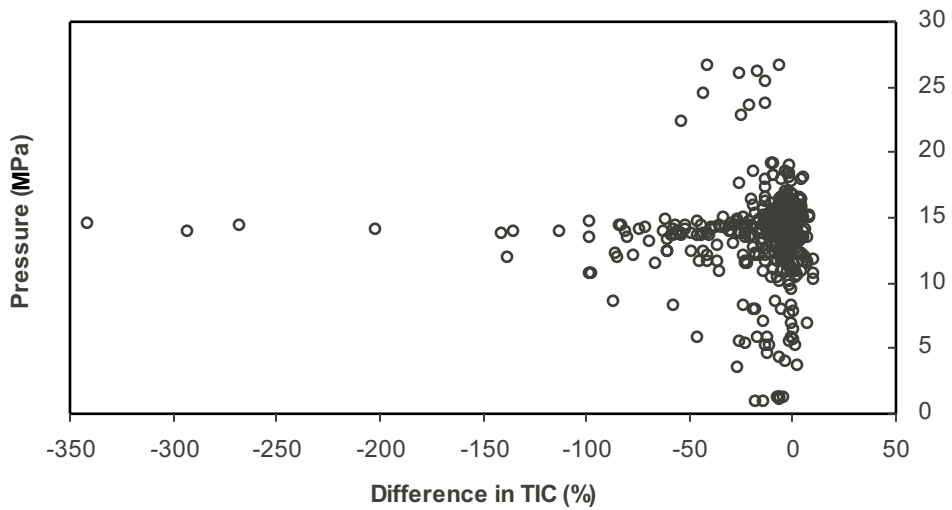
a.



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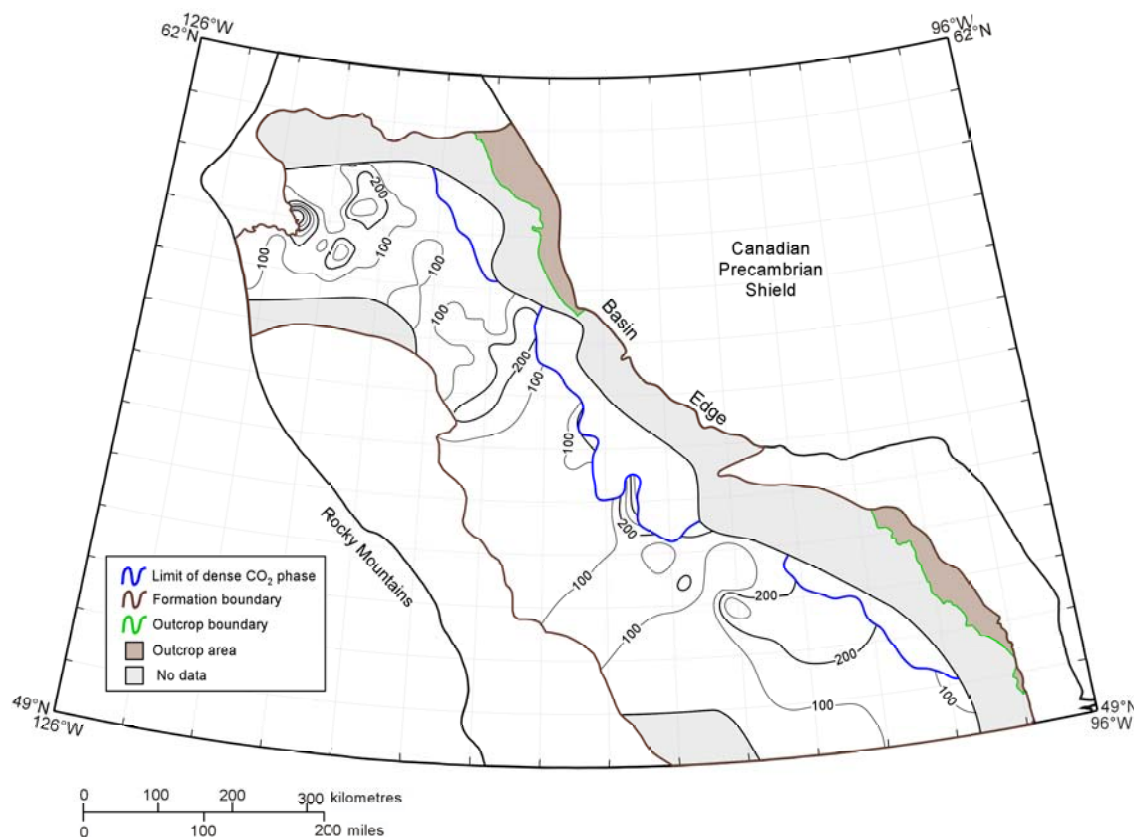


c.



**Figure 6. Variation with: a) salinity, b) temperature, and c) pressure, of the relative difference (%) between the in-situ total inorganic carbon (TIC) estimated using the Debye-Hückel and Pitzer geochemical speciation models, expressed as  $(TIC_{DH} - TIC_P)/TIC_{DH}$ .**

procedure presented previously for each data point, on the basis of water and CO<sub>2</sub> properties at that location, leading to values that vary between 17.4 and 73.9 kg/m<sup>3</sup> solution, with an average of 27.2 kg/m<sup>3</sup> solution. Figure 7 presents the variation in the ultimate CO<sub>2</sub>-sequestration capacity in solution in the formation water of the Winnipegosis aquifer.



**Figure 7. Areal distribution of the ultimate CO<sub>2</sub>-sequestration capacity in solution, UCSCS (kt/km<sup>2</sup>), in the Winnipegosis aquifer.**

The most important observation is that, for this aquifer characterized by very saline water, the difference between the current and maximum CO<sub>2</sub> content is between one and two orders of magnitude. As a result, the ultimate CO<sub>2</sub>-sequestration capacity in solution is determined mainly by the maximum CO<sub>2</sub> solubility at saturation in formation water, and depends negligibly on the current total inorganic carbon. Thus, a large difference in the current TIC calculated using the Debye-Hückel and Pitzer equations translates, nevertheless, into only very small differences in capacity. Bachu & Adams (2003) arrived at a similar conclusion for a sandstone aquifer in the Alberta basin located much higher up in the sedimentary succession, and whose water contains only up to 80 g/l total dissolved solids. Thus, it seems that achieving great accuracy in estimating the current TIC is not critical for estimating the ultimate CO<sub>2</sub>-sequestration capacity in solution, particularly if the data are incomplete or the computational effort is significant, as in the case of Pitzer equations.

Finally, the capacity of the entire Winnipegosis aquifer to sequester CO<sub>2</sub> dissolved in formation water is calculated considering its porosity and thickness (Figure 2) for the area that is suitable for CO<sub>2</sub> injection as a dense fluid (Figure 4). The capacity of formation waters to sequester CO<sub>2</sub> in solution varies between 0.01 and 0.75 Mt CO<sub>2</sub>/km<sup>2</sup> aquifer, with an areal average of 0.11 Mt CO<sub>2</sub>/km<sup>2</sup>. The ultimate CO<sub>2</sub>-sequestration capacity in solution in the Winnipegosis aquifer, UCSCS, is 66 Mt CO<sub>2</sub>. Similar calculations for the Viking aquifer in the Alberta basin indicate that the shallower Viking aquifer has a larger capacity for CO<sub>2</sub> sequestration in solution, estimated at ~100 Gt CO<sub>2</sub> (Bachu & Adams, in press),

although its areal extent is only one third of that of the Winnipegosis aquifer. The lower thickness of the Viking aquifer (about two thirds of that of the Winnipegosis aquifer) is compensated by its greater porosity (20% versus 10% on average). The main reason for the lower capacity for CO<sub>2</sub> sequestration in solution in the Winnipegosis aquifer is the significantly higher salinity of formation water (highest values >350 g/l) compared to a maximum of approximately 80 g/l in the Viking aquifer. The current analysis shows that formation water salinity is the most important factor in determining the capacity of an aquifer for CO<sub>2</sub> sequestration in solution in formation water. The results also show that aquifers in sedimentary basins have an extremely large capacity for sequestering CO<sub>2</sub>, orders of magnitude greater than oil and gas reservoirs.

## CONCLUSIONS

Geological sequestration of CO<sub>2</sub> is a means of reducing atmospheric emissions that is immediately available and technologically feasible. Deep saline aquifers may provide the largest capacity for CO<sub>2</sub> geological sequestration as a result of their size and wide distribution by comparison with other geological media such as hydrocarbon reservoirs. The ultimate CO<sub>2</sub>-sequestration capacity in solution (UCSCS) of an aquifer is the difference between the ultimate capacity for CO<sub>2</sub> at saturation and the total inorganic carbon currently in solution in that aquifer, and depends on formation water pressure, temperature and salinity.

Since there are no direct measurements of the total inorganic carbon (TIC), the current TIC content in formation waters can be calculated on the basis of standard analyses of formation waters collected by the energy industry during exploration for and production of hydrocarbons. Assuming non-reactive aquifer conditions, the current carbon content is evaluated on the basis of the concentration of carbonate and bicarbonate ions, and of the relations between the activities of these species at equilibrium at the conditions prevalent in the aquifer. Because formation water samples are analyzed at surface conditions, the analyses can be brought to in situ conditions using a geochemical speciation model, such as Pitzer and Debye-Hückel, to account for dissolved gases that are lost from the water sample. Both models were used to determine the activity coefficients for the Winnipegosis carbonate aquifer in the Western Canada Sedimentary Basin, which contains mostly brine. Significant differences in the calculated TIC values between these two models occur for highly saline waters (salinity >250 g/l), and generally for low TIC (<0.8 g/kg solution).

The maximum CO<sub>2</sub> content at saturation in formation water was calculated by estimating the CO<sub>2</sub> content at saturation in pure water and applying an empirical correction that takes into account the decrease in CO<sub>2</sub> solubility with increasing water salinity. The maximum CO<sub>2</sub> content at saturation is greater by 2 to 3 orders of magnitude than the current TIC, indicating that differences between the Pitzer and Debye-Hückel geochemical speciation models in estimating current TIC can be neglected. Furthermore, the current TIC can be neglected all together in most cases, greatly simplifying the calculations. The errors that would be introduced by neglecting the current TIC are well within the error introduced by data measurement, assumptions, algorithms and various extrapolations used in the estimates.

The ultimate CO<sub>2</sub>-sequestration capacity in solution in the Winnipegosis aquifer was calculated by considering the effect of dissolved CO<sub>2</sub> on formation water density, and aquifer thickness and porosity, to account for the volume of water in the aquifer pore space, and for the mass of CO<sub>2</sub> dissolved in water currently and at saturation. The aquifer, with an area of 615,000 km<sup>2</sup> in the region that is suitable for CO<sub>2</sub> sequestration, can sequester 27.2 kg CO<sub>2</sub>/m<sup>3</sup> solution, for a total of 66 Gt CO<sub>2</sub>. These calculations for just one aquifer in the Western Canada Sedimentary Basin show that deep saline aquifers have a huge capacity for sequestering CO<sub>2</sub>, and that the salinity of formation water is the most important factor in controlling the amount of CO<sub>2</sub> that can be sequestered in solution in deep saline aquifers.

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